VISUAL AND PHOTOMETRICAL TRACERS DETECTION OF RED COLOURANT IN OILFIELD WATER

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Chemical tracers can be used to keep track of drilling fluid distribution and find important applications in a number of fields including groundwater investigation and oil and gas exploration. The inorganic tracers including thiocyanate exhibit the advantages of simple hydrochemical behavior, simple composition, general insensitivity to environmental conditions and higher stability in drilling fluid as compared to organic dyes.

Thiocyanate is often avoided in field studies as its detection generally requires more complicated and off-site chemical analysis that may be impractical for field studies. Thiocyanate is an important tracer for oil reservoir monitoring, so its anion should be detected at any level. Colorimetric analysis with spectrophotometric detection is a simple, rapid and highly reproducible technique. The design of simple optical analytical systems represents an exciting area of research where everyday information technology and communication devices play an important role [4, 5]. The possibility of developing transparent polymer-based analytical devices has been recently demonstrated [2] and received an increasing attention as a method offering great opportunities for a wide variety of analytical applications.

However, its sensitivity is often insufficient to determine a target substance in real samples without the use of solid-phase extraction [1, 6]. One of them, transparent polymethacrylate polymer (TPP) consists of polymethacrylate (PMA) as a base polymer and polyethylene glycol (PEG) as a modifier with hydrophilic chains. Solid phase extraction of target substances using TPP can be achieved on the basis of almost the same mechanism as for the corresponding liquid–liquid extraction systems. Properties of TPP are easy to adjust for extraction of target substances by altering components of TPP. The TPP shaped as a flat sheet is used because it is a block polymerization product. Combined PMA and PEG matrices with polymethacrylate backbone and hydrophilic PEG chains have been synthesized and applied for manufacture of transparent color sensors. Solid-phase extraction using TPP has been used for determination of metal ions and organic substances [2, 3].

The proposed method is based on implementation of a well-known complexation reaction between thiocyanate CNS^- and Fe^{3+} with formation of the red color complex in the TPP plate under acidic conditions. The sensor turns red because of the formation of $Fe(CNS)_n$ complex. The color change is proportional to the concentration of thiocyanate in the solution (Fig. 1, 2).

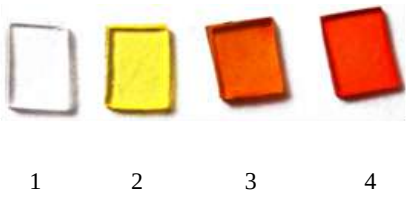

Fig 1. Scanned images of TPP: 1 – initial TPP with immobilized Fe^{3+}; TPP with immobilized Fe^{3+} after contact with 4 mg·L^{-1} (2), 20 mg·L^{-1} (3) and 30 mg·L^{-1} (4) thiocyanate solutions

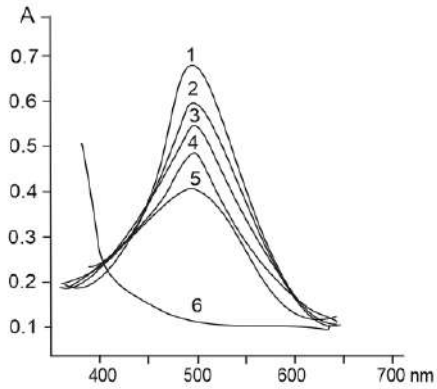

Fig. 2. Absorption spectra of Fe^{3+} immobilized into the TPP after reaction with various concentration of thiocyanate: 1 – 30 mg·L^{-1}; 2 – 20 mg·L^{-1}; 3 – 10 mg·L^{-1}; 4 – 4 mg·L^{-1}; 5 – 1 mg·L^{-1}; 6 – 0 mg·L^{-1}

TPP is a specially created material containing functional groups, which make it possible to extract a substance to be determined. The TPP plates were obtained through radical block polymerization (Agca et al., 1990). A colorimetric sensor is a plate sized 6.0 x 8.0 mm and weighs about 0.05 g. It is based on the polymethacrylate matrix containing immobilized Fe^{3+}. Immobilization of Fe^{3+} into TPP was performed through its sorption from 0.01 M water solution of $Fe(NO_3)_3$ during 2 minutes. As a result, we obtained a colorless sensing element for determination of thiocyanate. We used the blank TPP as a reference standard when measuring optical qualities of the TPP containing immobilized reagent after contact with the analyte solution.

One plate of TPP with immobilized Fe^{3+} was placed into a 250-ml flask containing 50 mL of pH 3.2 thiocyanate and citrated buffer solution and stirred for 15 minutes in a vibromixer, then removed and dried with filter paper. Optical density was measured in the maximum absorption of the Fe(III)-thiocyanate complex into the body of TPP at 490 nm.

In order to determine thiocyanate, we poured aliquots of oilfield water into 50-mL flasks, then added 10.0 mL of 0.1 mol·L^{-1} nitric acid changing the acidity to 3.2 pH and 1.0 mL of thiocyanate solution with accurate concentration, then diluted the mixture with distilled water to the mark. Next, the solutions were transferred to conical flasks, the PMM plates were plunged into these samples and the contents of the flasks were mixed using a vibratory mechanical agitator for 15

minutes, then the plates were taken out, dried between sheets of filter paper, and the absorption was measured at 490 nm. Thiocyanate concentration was determined according to the calibration dependence constructed in similar conditions in the concentration range of 0.5 to 30.0 mg·L^{-1}.

The linear concentration range was established between 0.8 and 30 mg·L^{-1}, with a regression coefficient of 0.9995 (Table 1). Color intensity of TPP is proportional to the target analyte concentration. The observations show that the color intensity is evenly distributed along the detection area. The detection limit of 0.3 mg·L^{-1} was calculated at a signal-to-noise ratio 3 under optimal conditions.

Table 1

Parameters of the analytical characteristics of the thiocyanate determination

Detection method	Linear range, mg·L^{-1}	Уравнение регрессии	LOD, mg·L^{-1}
Visual with TPP	6,0-20,0		6,0
Spectrophotometry with TPP	0,8-30,0	A=0,04565C + 0.06457 (R=0,99970)	0,3
Spectrophotometry with Fe^{3+} solution	2,0-40,0	A=0,14234C + 0.07346 (R=0,99904)	0,5

TPP completely extracts Fe^{3+} ions from the solution volume of 50 ml at a concentration below 0.002 M. The equilibrium is established in 10 minutes when the metal ion concentration is above 0.002 M. The extraction of metal ions into TPP is irreversible. This is probably due to donor-acceptor interactions between *d*-orbitals of Fe^{3+} and unshared pairs of electrons in the oxygen atoms. This creates some problems; for example, TPP can not be used for analytical methods involving target substance desorption.

The developed transparent polymer-based device was used for detection of thiocyanate in oilfield water. Accuracy of the methodology was validated using the standard addition method. Reproducibility was evaluated by repeating the proposed approach 6 times for each sample. Recovery of CNS^- in two samples of water with different concentrations based on the average of replicate measurements are illustrated in Table 2; the obtained results show that the proposed method is suitable for determination of CNS^- in such samples for the entire range of studied concentrations.

Table 2

Spectrophotometric determination of thiocyanate in oilfield water samples

CNS^- added, mg·L^{-1}	with TPP	with Fe^{3+} solution
	CNS^- found± SD, mg·L^{-1}	
Oilfield water (July), Oilfield Festivalnoye		
0	2.1±0.2	2.0±0.2
2	4.3±0.4	4.1±0.3
4	5.7±0.5	5.7±0.5
8	10.1±1.1	10.7±1.2
12	14.2±1.5	14.4±1.4
Oilfield water (August), Oilfield Sneznoye		
0	3.1±0.3	3.2±0.3
2	5.1±0.5	5.5±0.6
4	7.2±0.8	6.9±0.8
8	11.3±1.2	11.9±1.3
12	15.5±1.6	14.2±1.5

In order to assess the method's accuracy, relative deviations between the expected and the obtained concentrations were calculated after spiking the sample with CNS^-. The spectrophotometric determination of CNS^- with Fe^{3+} solution is recognized as a reference method for measuring thiocyanate in oilfield water and should always be seen as a backup method to any alternative method. The colorimetric sensor we developed is a convenient, practical and simple device for monitoring thiocyanate. Solid phase extraction of CNS^- into TPP can be completed and transported without concern for sample stability.

References

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